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SINGLET→TRIPLET ABSORPTION IN HALOGEN SUBSTITUTED TOLUENES*

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ABSTRACT. Continuous singlet→triplet absorption in the near ultraviolet region due to orthobromotoluene, parachlorotoluene and metafluorotoluene in the liquid state has been investigated. It has been observed that the region of absorption shifts gradually towards the red with the increase in the atomic weight of the substituent halogen atom. The luminescence spectrum due to metafluorotoluene in the solid state at −180°C has also been studied, and the luminescence bands have been found to be weaker than those due to chloro- and bromotoluene.

INTRODUCTION

It is well known that Lewis and Kasha (1944) first suggested that the phosphorescence exhibited by many pure substances are due to transitions from the triplet state of the molecules to the lowest singlet state. Lewis and Kasha (1945) also observed singlet→triplet (S→T) absorption in pure para dichlorobenzene, dibenzalacetone, nitrobenzene and phenazine. Reid (1950a) next observed (S→T) absorption bands in pyridine in the liquid state at room temperature and in ethylene in the vapour state (Reid, 1950b). Later, Kasha (1952) demonstrated that the singlet→triplet absorption in aromatic compounds is strengthened not only by heavy substituent atoms in the molecule but also by such atoms in surrounding solvent molecules in any solution. McClure *et al.* (1954) observed S→T absorption in para diiodobenzene, para dibromobenzene, bromobenzene, β-iodochloro-and β-iodobromo naphthalenes, 1, 3, 5-tribromobenzene and 1, 2, 4, 5-tetrabromobenzene, but they did not find any such absorption in para dichlorobenzene, para iodobiphenyl and nitrobenzene either at the room temperature or at liquid nitrogen temperature. The apparent non-appearence of any S-T bands in the above cases was attributed by them to the difficulties of separating the very weak and diffuse S→T absorption spectra from the normal singlet→singlet absorption. Biswas (1954, 1955a & b, 1956a & b) and Sirkar and Biswas (1956) observed luminescence bands in some halogen substituted toluenes and although Biswas (1956) looked for the absorption band responsible for the emission he was

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unable to detect any strong S→T absorption. Recently, it has been shown by the present author (Roy, 1959) that the luminescence in parachlorotoluene in the solid state at −180°C takes place after direct S −T transition.

It was thought worthwhile to investigate whether any singlet→triplet absorption is exhibited by these compounds and whether the intensity of such absorption depends on the atomic weight of the heavy substituent atom in the molecule as reported by previous workers in other cases (McClure, *et al.* 1954). In the present investigation the singlet→triplet absorption in metafluorotoluene, parachlorotoluene and ortho bromotoluene have been studied using a long absorbing path.

The luminescence spectrum of pure metafluorotoluene in the solid state at −180°C has also been investigated and it has been compared with the spectra due to chlorotoluenes and bromotoluenes reported by previous workers (Biswas, 1956a & b).

EXPERIMENTAL

The liquids orthobromotoluene, parachlorotoluene and metafluorotoluene of chemically pure quality supplied by British Drug House (England), were distilled several times under reduced pressure and fractionated to remove traces of impurities. For studying the absorption spectra of the above substances in the liquid state at 24°C, a 10 cm. long pyrex glass cell provided with plane parallel quartz windows was used. A 250 watt straight filament lamp in glass envelope was employed as the source of continuous radiation in the near ultraviolet region. The absorption spectra of the substances were photographed on Ilford HP3 films using a Hilger medium quartz spectrograph having a dispersion of 22 Å/mm in the 3500 Å region. The time of exposure varied from a few seconds to half a minute and the width of the slit was about 0.10 mm. Iron arc spectrum was recorded on each spectrogram as comparison. The absorption spectrum of benzene was also recorded for comparing it with the spectra of the disubstituted benzenes mentioned above. The microphotometric records of the spectrograms were obtained with a self-recording Moll microphotometer supplied by Kipp and Zonen. The absorption spectra were calibrated with the help of the microphotometric records of the iron lines after drawing a thin and straight reference line across the spectra, coinciding with a known iron line.

The luminescence spectrum of pure meta fluorotoluene in the solid state at −180°C was investigated with the arrangements used previously by Biswas (1956a).

RESULTS AND DISCUSSION

The microphotometric records of the absorption spectra due to pure orthobromotoluene, parachlorotoluene, metafluorotoluene and benzene are reproduced

in Figs. 1(a), 1(b), 1(c) and 1(d) respectively. The reference line in the records is the 4046 Å line of mercury.

The main bands in the luminescence spectrum due to metafluorotoluene in the solid state at −180°C with their widths and estimated intensities (*s*—strong, *m*—medium, *w*—weak, etc.) are given in Table I.

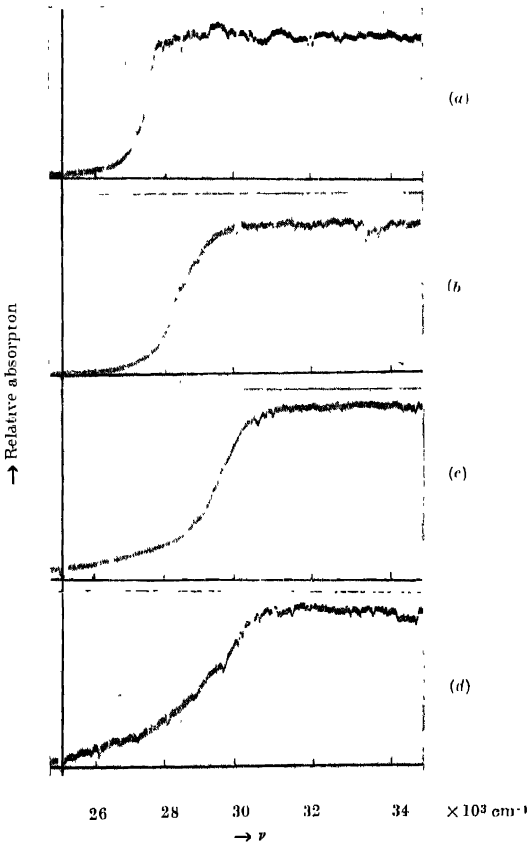

Fig. 1. (*a*) *o*-Bromotoluene (*b*) *p*-Chlorotoluene
(*c*) *m*-Fluorotoluene, (*d*) Benzene

TABLE I

uce spectra of metafluorotoluene a

Position of the bands ν in cm^{-1}	Width of the bands in cm^{-1}	Differences from the 1st band in cm^{-1}
24968 (w)	436	
24072 (w)	725	896
23413 (s)	603	1555
22521 (m)	558	2447
21761 (s)	948	3207
20910 (vw)	765	4058

DISCUSSION

(a) *Absorption spectra due to singlet → triplet transition.*

It is well known (Lewis and Kasha, 1945) that benzene shows a weak S→T absorption in the region (3300-3700)Å. This is evident from Fig. 1(d). The absorption due to metafluorotoluene reproduced in Fig. 1(c) appears to be similar to that due to benzene (Fig. 1(d)). This similarity indicates the existence of very weak S→T absorption in metafluorotoluene. Fig 1(b) and 1(a) show that as the fluorine atom is replaced successively by chlorine and bromine atoms, the S→T absorption becomes much stronger and the region where the absorption starts shifts gradually towards red. Further, absorption curves due to orthobromotoluene and parachlorotoluene show steeper rise in this region than in the case of either metafluorotoluene or benzene. These results are similar to those reported by McClure *et al.* (1954) for substituted napthalenes. It is evident from results of the present investigation that in the case of substituted benzenes also the perturbation due to substituent halogen atom increases with the increase in the atomic weight of the substituent atom and the S→T transition becomes allowed.

The strong S→T absorption observed in the cases of orthobromotoluene and parachlorotoluene also explains the intense luminescence in the visible region exhibited by these compounds in the solid state at −180°C (Biswas, 1956a, 1956b).

(b) *Luminescence spectrum of metafluorotoluene.*

It would be interesting to compare the intensities of luminescence spectrum of metafluorotoluene with that due to orthobromotoluene or parachlorotoluene excited under similar conditions. It can be seen from the results obtained by Biswas (1956 a & b) that the intensity of luminescence spectrum of orthobromo-

toluene is larger than that due to parachlorotoluene. The intensity of the luminescence spectrum due to metafluorotoluene recorded under similar conditions has been found to be lower than that due to para chlorotoluene. This agrees with the fact that the strength of S→T absorption is small in this case and shows further that the luminescence is produced by the transition from the triplet to the singlet state.

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